EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100786

Chemistry Europe
European Chemical Societies Publishing

Oxidative Addition of Secondary Phosphine Oxides through Rh(I) Center: Hydrido-Phosphinito-Rh(III) Complexes and their Catalytic Activity in Hydrophosphinylation of Alkynes

Naroa Almenara,[a] Montserrat Barquin,[a] Miguel A. Huertos,*[a, b] and María A. Garralda*[a]

The reaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ with diimines, differing in their steric and electronic properties, and with diphenylphosphine oxide leads to the oxidative addition products, hydrido-phosphinito-Rh(III) complexes $\{Rh(PPh_2OH)(PPh_2O)(NN)(H)Cl\}$ (**1**), stabilized by the formation of a hydrogen bonded phosphinous acid-phosphinito quasi-chelate [(PO···HOP)-κ^2P]. Exchange of hydride by chloride to afford $\{Rh(PPh_2OH)(PPh_2O)(NN)Cl_2\}$ (**2**) occurs in hydrido complexes containing low steric hindrance diimines and is inhibited for complexes containing encumbered diimines. Complexes **1** react with $BF_3{\cdot}OEt_2$ with exchange of the acidic proton by BF_2, and transformation of the quasi-chelating PO···HOP into a chelating PO-BF_2-OP ligand in $\{Rh\{(PPh_2O)_2BF_2\}(NN)(H)Cl\}$ (**3**). The reaction of $[Rh(\mu\text{-}Cl)(nbd)]_2$ or [Rh(acac)(nbd)] with diphenylphosphine oxide leads to coordinatively unsaturated nortricyclyl-phosphinito-Rh(III) complexes, $\{Rh(PPh_2OH)(PPh_2O)(ntyl)(\mu\text{-}Cl)\}_2$ (**4**) or $\{Rh(PPh_2OH)(PPh_2O)(ntyl)(acac)\}$ (**6**), respectively. Their reaction with $BF_3{\cdot}OEt_2$ results in the corresponding $\{Rh\{(PPh_2O)_2BF_2\}(ntyl)(\mu\text{-}Cl)\}_2$ (**5**) or $\{Rh\{(PPh_2O)_2BF_2\}(ntyl)(acac)\}$ (**7**). Some of these new complexes have shown catalytic activity in hydrophosphinylation of alkynes, with $\{Rh(PPh_2OH)(PPh_2O)(NN)(H)Cl\}$ containing encumbered NN being efficient and regioselective catalysts in the hydrophosphinylation of phenylacetylene with diphenylphosphine oxide to produce (*E*)-diphenyl(styryl)phosphine oxide.

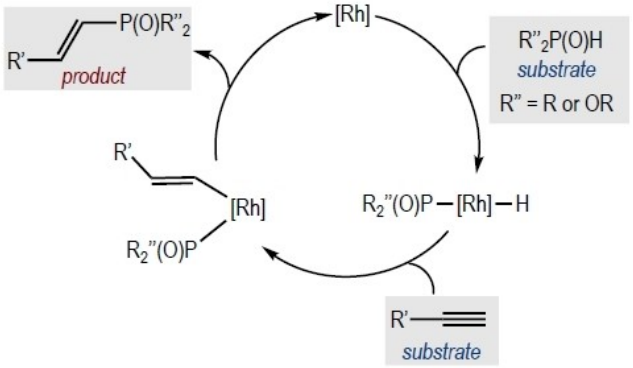
Introduction

Secondary phosphine oxides, air and moisture stable, exist as two tautomers in equilibrium, the pentavalent $R^1R^2P(=O)H$ (SPO) and the trivalent phosphinous acid $R^1R^2P(OH)$ (PA). The transition metals O-coordination of SPOs or P-coordination of PAs or their anion phosphinito ($R^1R^2PO^-$), together with the strong hydrogen bonded mixed system $[R^1R^2PO{\cdots}HOPR^1R^2]$, afford versatile catalysts for a variety of reactions that nowadays are well known.[1] For simple aromatic and aliphatic substituents the tautomeric equilibrium favors the SPO form. Theoretical studies on the tautomerism suggest a bimolecular mechanism via P···H···O···P or mononuclear solvent-assisted hydrogen bonding as most likely and metal atoms may favor the tautomerization as consequence of PA coordination.[2] In the presence of Ru(II) complexes, an easier tautomerism for $H_n(OH)_{3-n}P(O)$ species has been proposed to occur via SPO O-coordination followed by P–H oxidative addition and Ru–to–O hydrogen transfer to afford P-coordinated PA species.[3] Among others, PA complexes have proven efficient in processes such as nitrile hydration to afford amides that may involve intramolecular addition of the hydroxyl group of the PA ligand to the metal-coordinated nitrile;[4] PA assisted C–H activation for arylation or hydrocarbamoylation reactions,[5] or hydroformylation and hydrogenation reactions with the latter ligand playing a role in heterolytic splitting of hydrogen.[6] Recently SPOs have been successfully used for nanoparticle stabilization showing efficient catalytic activity.[7]

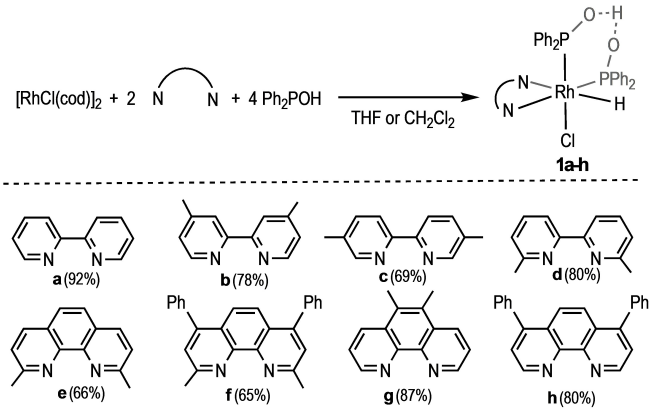
The hydrophosphinylation of alkynes using SPOs may lead to the formation of vinylphosphine oxides important as biologically active molecules, as additives or flame-retardants in material science applications and as useful precursors for asymmetric addition reactions.[8] In the nineties Tanaka et al. developed the first efficient Pd-catalyzed regio- and stereoselective hydrophosphinylation of alkynes,[9] and subsequent studies were reported on the efficient terminal alkynes hydrophosphinylation catalysed by several rhodium complexes.[10–11a] More sustainable transition-metals such as nickel[12] and copper[13] are also effective for H–P(O) additions to alkynes and recently the corresponding radical promoted reactions assisted by photoirradiation or radical initiators has been studied.[14] The proposed mechanism for the production of vinylphosphorus derivatives catalysed by rhodium compounds, shown in Scheme 1,[8d,15] includes as first step an oxidative addition into the Rh(I) complex leading to the formation of hydrido-phosphinito-Rh(III) type compounds.

[a] N. Almenara, Dr. M. Barquin, Dr. M. A. Huertos, Prof. M. A. Garralda
Departamento de Química Aplicada
Universidad del País Vasco (UPV/EHU)
Apartado 1072, 20080, San Sebastián, Spain
E-mail: miguelangel.huertos@ehu.es
mariaangeles.garralda@ehu.eus
[b] Dr. M. A. Huertos
IKERBASQUE, Basque Foundation for Science
48013, Bilbao, Spain

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202100786



Scheme 1. Proposed catalytic cycle for the hydrophosphinylation of alkynes.



Scheme 2. Synthesis of complexes **1 a**–**h**. In THF (**1 a**–**d**) or in CH_2Cl_2 (**1 e**–**h**).

The reaction of $RhCl(PPh_3)_3$ with phosphonates, $P(OR)_2(O)H$, allowed the isolation of the hydrido-phosphonate-Rh(III) complex $[RhH(Cl)(PPh_3)_2\{(P(OR)_2O)_2H\}]$, which was proposed as intermediate in the hydrophosphorylation of alkynes and provided experimental evidence for this oxidative addition step.[15] Nevertheless, formation of analogous rhodium complexes using secondary phosphine oxides appears unusual, as rhodium(I) complexes react usually maintaining their oxidation state. For example, the reaction of an excess of $PPh_2(O)H$ with $[Rh(\mu\text{-}Cl)(cod)]_2$ (cod = 1,5-cyclootadiene) resulted in the formation of the Rh(I) complex $[RhCl(PPh_2(OH))_2(PPh_2(O)H)_2]$ and $(C_2F_5)_2POH$ led to $[Rh\{(P(C_2F_5)_2O)_2H\}(cod)]$.[11] $[Rh(\mu\text{-}Cl)(CO)_2]_2$ reacted with $PMe^tBu(O)H$ to afford $[RhCl(CO)(PMe^tBu(OH))_2]$.[16] The reaction of $PR_2(O)H$ with [Rh(acac)(cod)] (acac = acetylacetonate) led to formation of the quasi-bidentate Rh(I) complex, $[Rh\{(PR_2O)_2H\}(cod)]$[17] and $[Rh(cod)_2]OTf$ afforded $[Rh\{(PR_2(OH))_2OTf\}(cod)]$.[18] Only recently the oxidative addition of $PPh_2(O)H$ to $[RhTp(C_2H_4)(PHPh_2)]$ (Tp = hydridotris(pyrazolyl) borato) has been reported to afford $[RhTp(H)(PHPh_2)(POPh_2)]$.[19] Oxidative addition of SPOs affording hydrides is well known for Pt(0) or Pd(0) and less frequent for Ni(0) or Ir(I).[2b, 9, 12, 20] DFT calculations indicate available transition states involving H–P(O) or H–OP bond activation depending on the metal and/or the SPO.[20]

Herein, we report on hydrido-diimine-Rh(III) compounds containing the $(Ph_2PO\cdots H\cdots OPPh_2)$-$\kappa^2$P system obtained through oxidative addition of diphenylphosphine oxide at Rh(I) complexes and on their reactivity towards hydride or proton abstractors. This kind of hydrido-complexes could be intermediates in alkyne hydrophosphinylation reactions.

Results and Discussion

Synthesis of hydrido complexes

Reaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ with 4 equivalents of diphenylphosphine oxide in the presence of 2 equivalents of 2,2′-bipyridine (bipy, **a** in Scheme 2) in THF at room temperature yielded the neutral hydrido-Rh(III) complex $[Rh(Cl)H\{(PPh_2O)_2H\}(bipy)]$ (**1 a**) (Scheme 2). The formation of complex **1 a** can be explained by oxidative addition of diphenyl phosphine oxide through [RhCl(cod)(bipy)], formed upon addition of bipyridine to the starting dimer rhodium(I) complex, with cod displacement. The resulting phosphinito-hydrido-Rh(III) complex appears stabilized by formation of a quasi-chelate ligand between the P-coordinated phosphinite and a P-coordinated phosphinous acid. We believe that the presence of the chelating heterocyclic N-donor ligand coordinated to rhodium favors both the oxidative addition reaction and the stability of the rhodium(III) complex. In the absence of bipyridine the reaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ with diphenylphosphine oxide led to intractable mixtures of complexes.

The characterization of **1 a** was performed in solution by NMR spectroscopy and ESI-MS. The analytical data agree with the proposed stoichiometry. A resonance in the high field region of the ^1H NMR spectrum of compound **1 a** is assigned to the hydride resulting from the P–H activation by the metal center. A doublet of triplets, due to coupling to two non-equivalent phosphorus atoms and to rhodium as indicated by ^1H NMR ($\delta = -13.96$ (dt, $J_{P\text{-}H} = 33$, $J_{Rh\text{-}H} = J_{P\text{-}H} = 17$ Hz)) is observed. The ^1H NMR spectrum at room temperature shows also the signals due to the bipyridine ligand coordinated to the rhodium atom. Lowering the temperature down to −60 °C, the ^1H NMR shows a sharp resonance at $\delta = 16.59$ indicating an intramolecular hydrogen bond and formation of a quasi-chelate containing the PO···HOP fragment, usually unobservable at room temperature.[17] Accordingly, the $^{31}P\{^1H\}$ NMR spectrum shows two doublets of doublets at 96.6 ppm (dd, $J_{Rh\text{-}P} = 134$ Hz, $J_{P\text{-}P} = 31$ Hz) and 90.0 (dd, $J_{Rh\text{-}P} = 127$ Hz, $J_{P\text{-}P} = 31$ Hz) that indicates two mutually cis non-equivalent phosphorus atoms. For **1 a** ESI-MS shows a strong molecular ion at m/z = 663.08, which agrees with $[RhH\{(PPh_2O)_2H\}(bipy)]^+$ (calc. for $[M-Cl]^+$ 663.08) and suggests **1 a** to be a mononuclear hexacoordinated 18e species. The IR spectrum shows a band at 2081 cm^{-1} due to ν(Rh–H), in the range expected for a hydride trans to bipyridine[21] and a stretching at 1097 cm^{-1}, in the ν(P=O) range.[22] Compound **1 a** was also characterized by single crystal X-ray structural determination (Figure 1). The geometry about

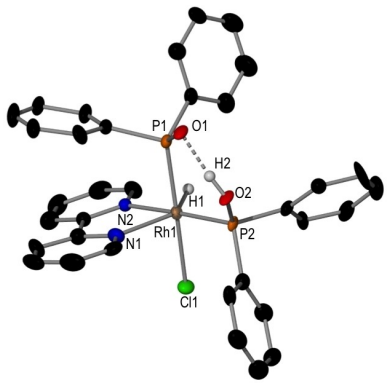


Figure 1. Molecular structure of **1 a**. Displacement ellipsoids are drawn at 50 % probability level. Most of the hydrogen atoms and crystallization solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–Cl1, 2.435(2); Rh1–P1, 2.259(2); Rh1–P2, 2.257(2); P1–O1, 1.546(6); P2–O2, 1.573(6); O1–O2, 2.445(8); Rh1–N1, 2.175(8); Rh1–N2, 2.125(6); P1–Rh1–Cl1, 175.04(8); P1–Rh1–P2, 90.95(8).

the Rh(III) center can be described as distorted octahedral with the apical positions occupied by chloride and one of the phosphorus atoms and the equatorial positions occupied by the bipyridine ligand, the other phosphorus atom and the hydride. In **1 a** the Rh–P bond distances are not significantly different [Rh1–P1, 2.259(2) and Rh1–P2, 2.257(2) Å], whereas the P–O bond distances are slightly different [P1–O1, 1.546(6) and P2–O2, 1.572(6) Å], and fall in between the typical ranges of a single and a double bond.[17,22] The O1···O2 distance of 2.445(8) Å reflects the existence of a strong PO···H–OP hydrogen bond.[23] The Rh–N bond distances are significantly different [(Rh1–N1, 2.175(8) and Rh1–N2, 2.125(6) Å] on account of the higher trans influence of the hydride.

We have extended this study to the reactions of $[Rh(\mu\text{-}Cl)(cod)]_2$ with $PPh_2(O)H$ in the presence of other heterocyclic diimines (NN), namely dimethyl-2,2′-bipyridines (**b**–**d**) and dimethyl- and/or diphenyl-substituted 1,10-phenanthrolines (phen, **e**–**h**) shown in Scheme 2. The corresponding neutral Rh(III) complexes $[Rh(Cl)H\{(PPh_2O)_2H\}(NN)]$ (**1 b**–**1 h**) (Scheme 2) were obtained in all cases and were characterized in solution by NMR spectroscopy and ESI-MS. The ^1H NMR spectra, showing analogous features to those of **1 a**, reflected also the non-equivalence of the two fragments of the NN-chelate. For complexes **1 a**–**1 d**, the resonance due to the hydride appears in the −13.90 to −14.51 ppm range. The highest field value, −14.51 ppm, corresponds to complex **1 d** (NN = 6,6′-Me_2-bipy), suggesting a decreased donor strength of the bulky ligand in this complex, most likely related to its steric hindrance. This feature is also observed for complexes **1 e**–**1 h** (−13.47 to −14.11 ppm range for the hydride), with complex **1 e**, containing the most basic and encumbered ligand (NN = 2,9-Me_2-phen), showing the hydride signal also at the highest field, −14.11 ppm. The resonance due to the hydrogen bridge, at low field, was observable only at low temperature (−60 °C). The $^{31}P\{^1H\}$ NMR spectra show the expected signals due to two non-equivalent phosphorus atoms mutually cis-coordinated. One of these resonances appears in all complexes **1 b**–**1 h** as doublet of doublet in the 98 to 92 ppm range. The signal due to the second phosphorus atom appears in the 93 to 90 ppm range for complexes **1 b**, **1 c**, **1 g** and **1 h**, while for complexes **1 d**, **1 e** and **1 f**, containing the o-dimethyl-substituted ligands, the corresponding resonance appears remarkably displaced towards higher field, in the 78 to 72 ppm range, and may be related to the steric hindrance of these ligands. The ESI-MS obtained for compounds **1 b**-**1 h** are in good agreement with the proposed structures (see Sup. Info. for more details). The IR spectra show a stretching in the ν(P=O) range, in the 1094 to 1098 cm^{-1} range. The band due to ν(Rh–H) appears as expected for a rhodium-bonded hydride trans to bipyridine,[21] but for complexes **1 d** and **1 e**, appearing at higher frequency, 2195 and 2166 cm^{-1}, respectively. A correlation frequently observed in transition metal hydrides[24] is thus found between δ(Rh–H) and ν(Rh–H), which could indicate a lower σ-donor strength of the bulkier ligands. Compound **1 e** was also characterized by single crystal X-ray structural determination (Figure 2), confirming a solid state structure of **1 e** in good agreement with that proposed on spectroscopic grounds in solution. The coordination geometry for the Rh(III) center is pseudo octahedral, with the hydride and a hydrogen bonded quasi-chelate ligand consisting of a phosphinous acid and a phosphinito ligand PO···HOP spanning one of the octahedron faces. The equal Rh–P bond distances are as those observed in **1 a**, while the difference between the P–O bond distances (P1–O1, 1.544(2); P1–O2, 1.581(2) Å) is slightly larger than in **1 a**. The O–H bond distances are also different, with the longer value associated to the shorter P–O distance (O1···H2, 1.57 (7); O2–H2, 0.99 (5) Å). The O1···O2 distance of 2.466(5) Å and the O1···H2–O2, 172(7)° angle agree with the existence of a strong hydrogen bond. The other octahedral face is occupied by the 2,9-Me_2-phen ligand and the chlorine.

The Rh–N bond distances are significantly different on account of the higher trans influence of the hydride (Rh1–N1, 2.251(2); Rh1–N2, 2.141(2) Å). For the trans to hydride Rh1–N1

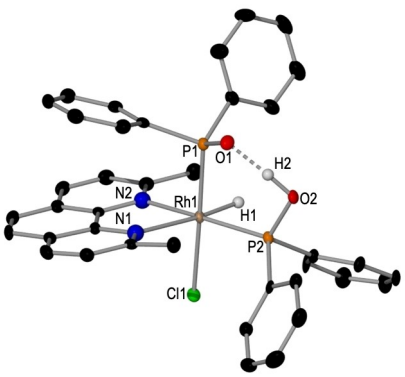


Figure 2. Molecular structure of **1 e**. Displacement ellipsoids are drawn at 50 % probability level. Most of hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°): Rh1–Cl1, 2.453(1); Rh1–P1, 2.255(1); Rh1–P2, 2.259(1); Rh1–H1 1.48(6); P1–O1, 1.544(2); P2–O2, 1.581(2); O1–H2, 1.57(7); O2–H2, 0.99(5); O1–O2, 2.466(5); Rh1–N1, 2.251(2); Rh1–N2, 2.141(2); P1–Rh1–Cl1, 177.81(5); N1–Rh1–P2, 168.01(1); H1–Rh1–N2, 173(2), P1–Rh1–P2, 91.65(3); O1–H2–O2, 172(7).

distance, we observe a remarkable difference between this complex **1e** and complex **1a** (Rh1–N1 of 2.175(8) Å). This longer Rh1–N1 bond distance in **1e** is in accordance with a lower σ-donor strength of the ligand as suggested by δ(Rh–H) and ν(Rh–H).

Exchange reactions in complexes 1

Some of these hydrido complexes **1** show catalytic activity in hydrophosphinylation of phenylacetylene (*vide infra*) and this prompted us to study hydride or proton exchange reactions to gain insight into their relevance in the catalytic activity.

Complexes **1a-c** and also complexes **1g–h** undergo exchange of hydride by chloride in chlorinated solvents to afford complexes **2a–c** and **2g-h** as shown in Scheme 3. This behavior has several precedents and exchange of hydride by chloride in hydrido-chloride-rhodium(III) complexes containing N-donor ligands has been frequently observed.[25] The quantitative synthesis of complexes **2a–c** and **2g–h** was performed stirring a CH_2Cl_2 or $CHCl_3$ solution of the corresponding complex **1** during several days. At variance with this behavior, complexes **1d–f**, containing the bulkiest NN ligands, 6,6′-Me_2-bipy (**d**), 2,9-Me_2-phen (**e**) or 2,9-Me_2-4,7-Ph_2-phen (**f**), are stable in chlorinated solvents and fail to undergo the hydride/chloride exchange reaction under analogous reaction conditions. We believe this is due to steric hindrance of the methyl groups inhibiting chloride approaching the rhodium atom. The neutral complexes were characterized by NMR and IR spectroscopies and ESI-MS. Single-crystal X-ray diffraction was performed on complexes **2a** and **2b**. The IR spectra show a stretching in the ν(P=O) range, in the 1095 to 1097 cm^{-1} range. The structures in the solid state (Figure 3a for **2a** and 3b for **2b**) consist of a Rh(III) centre in a pseudo-octahedral geometry. Two positions of the equatorial plane are occupied by the bipy ligand. In *trans* position to the corresponding nitrogen atoms a chlorine atom and a phosphorus atom are located. Finally, the other chloride and phosphorus atoms occupy the apical positions of the octahedron. The Rh–N bond distances reflect the higher *trans* influence of phosphorus compared to that of chloride, and the Rh–P bond distances are slightly different. In both complexes the quasi-chelate ligand bounded by a hydrogen bridge PO···HOP between formally a phosphinous acid and a phosphinite is observed. For complex **2a** with slightly different P–O bond distances (P1–O1, 1.532(3); P2–O2, 1.575(3) Å), O1···H01 = 1.49(5) Å and O2–H01 = 0.97(5) Å are found. In complex **2b**, with closer P–O bond distances (P1–O1, 1.547(3); P2–O2, 1.558(3) Å), O1–H01 = 0.922(10) Å and O2···H01 = 1.479(11) Å distances are observed. In both cases the O···O distance (2.464(4) and 2.399(4) Å) and the O1–H01–O2 angle (171(4) and 175.94(29)°) reflect a strong hydrogen bond.

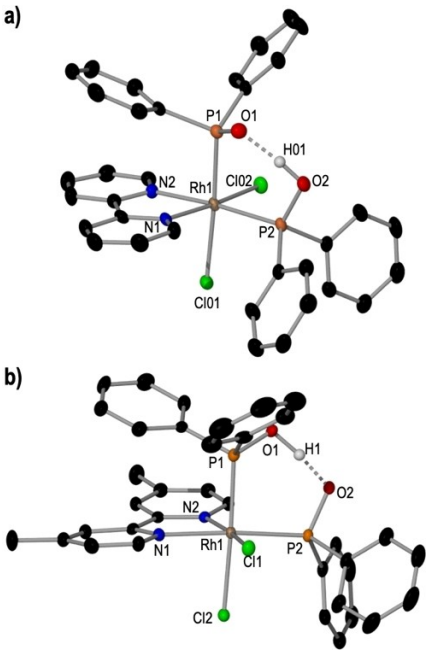
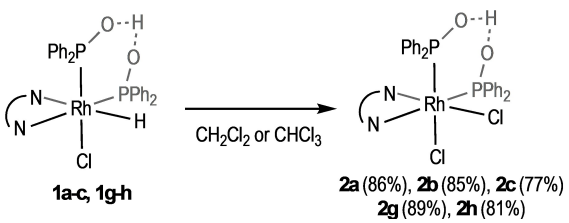


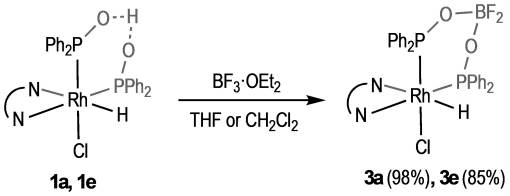
Figure 3. a) Molecular structure of **2a**. Displacement ellipsoids are drawn at 50% probability level. Most of hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°): a) Rh1–Cl01, 2.4676(9); Rh1–Cl02, 2.3291(8); Rh1–N1, 2.077(3); Rh1–N2, 2.132(3); Rh1–P1, 2.2845(9); Rh1–P2, 2.3097(9); P1–O1, 1.532(3); P2–O2, 1.575(3); O1–H01, 1.49(5); O2–H01, 0.97(5); O1–O2, 2.464(4), Cl1–Rh1–P1, 176.76(3); P1–Rh1–P2, 91.51(3). O1–H01–O2, 171(4). b) Molecular structure of **2b**. Displacement ellipsoids are drawn at 50% probability level. Most of hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°). b) Rh1–Cl1, 2.3319(9); Rh1–Cl2, 2.4542(9); Rh1–N1, 2.124(3); Rh1–N2, 2.057(3); Rh1–P1, 2.2877(9); Rh1–P2, 2.3208(9); P1–O1, 1.547(3); P2–O2, 1.558(3); O1–H1, 0.922(10); O2–H1, 1.479(11); O1–O2, 2.399(4), P1–Rh1–Cl2, 177.43(3), P1–Rh1–P2, 92.25(3); O1–H1–O2, 175.194(29).

The characterization of compounds **2** in solution is in good agreement with the structures obtained in the solid state. The ESI-MS of compounds **2** agree with the corresponding $[Rh(Cl)\{(PPh_2O)_2H\}(NN)]^+$. The ^1H and $^{13}C\{^1H\}$ NMR spectra show the expected features. In the $^{31}P\{^1H\}$ NMR spectra, a significant shift of the resonances towards higher fields is observed upon H/Cl exchange. Complexes **2** show two doublets of doublets due to two mutually *cis* phosphorus atoms in the 75–72 and 69–68 ppm ranges. (see Sup. Info. for more details)

The bridging protons in the phosphinito-phosphinous acid "quasi-chelate" can be readily substituted by BF_2 giving complexes containing a chelating $[R_2PO(BF_2)OPR_2]$ structure. Such rhodium,[17, 26] iridium,[26a] palladium[27], platinum[28] and nickel[29] complexes are known. The addition of an excess of $BF_3{\cdot}OEt_2$ to THF solutions of $[Rh(Cl)H\{(PPh_2O)_2H\}(NN)]$ (**1**) afforded compounds $[Rh(Cl)H\{(PPh_2O)_2BF_2\}(NN)]$ (NN = bipy, **3a**; 2,9-Me_2-phen, **3e**), shown in Scheme 4.



Scheme 3. Synthesis of complexes **2a–c** in CH_2Cl_2 and **2g–h** in $CHCl_3$.



Scheme 4. Reactivity of compounds **1** with $BF_3 \cdot OEt_2$. Synthesis of complex **3a** in THF and **3e** in CH_2Cl_2.

Complexes **3** were characterized in solution by NMR spectroscopy and ESI-MS that agree with the proposed structure. In the ^{1}H NMR spectra the doublet of triplet due to the hydride at −13.58 ppm for complex **3a**, appears at lower field than for **1a** (−13.90 ppm). For **3e**, with a hindered NN ligand, the corresponding resonance at −14.79 ppm appears displaced to higher field respect to **1e** (−14.11 ppm). In the ^{31}P{^{1}H} NMR spectra downfield shifts of 14 or 8 ppm, respectively for the lower and higher field resonances are observed. In the ^{11}B spectra, a single signal at 1.1 ppm agrees with a PO–BF_2–OP Rh-chelate. Finally, the ^{19}F spectra show two signals at −131.1 (bd, $J_{F\text{-}F}$ = 69 Hz) and −133.9 (bd, $J_{F\text{-}F}$ = 70 Hz) that agree with two diastereotopic fluorine atoms.[30] In the IR spectrum of **3e** the ν(Rh–H) stretching appears at remarkable high frequency, 2213 cm^{-1}, in accordance with the high field δ(Rh–H).

Determination of the solid-state structure of compound **3a** was also possible using X-ray diffraction. The resulting structure agrees with that deduced from the spectroscopic data in solution (Figure 4). The Rh(III) center sits in a distorted octahedral geometry. The new PO–BF_2–OP ligand is coordinated as bidentate via the two PPh_2 moieties (Rh1–P1, 2.233(2); Rh1–P2, 2.249(1) Å) to form a six-membered ring chelate. The P–O bond distances are equally long in **3a**, P1–O1, 1.570(4) Å and P2–O2, 1.574(5) Å. As reported for related Pt(II) complexes,[28c] replacing of the hydrogen bond in **1a** by BF_2 is not reflected by a substantial lengthening of the P–O bonds. The chloride and a nitrogen atom (N2) of the bipy are located trans to the phosphorus atoms. The remaining two positions are occupied by mutually trans hydride and nitrogen (N1) atoms.

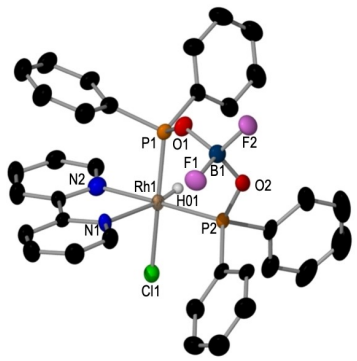
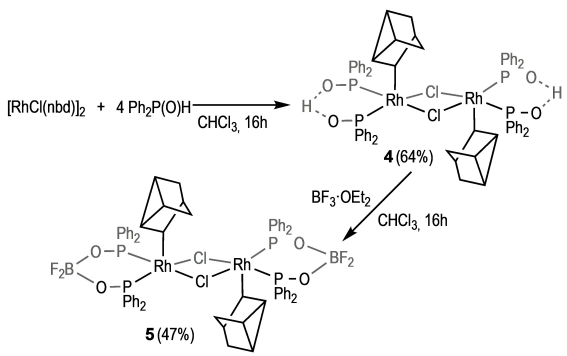


Figure 4. Molecular structure of **3a**. Displacement ellipsoids are drawn at 50% probability level. Most of hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°): Rh1–H01, 1.398(10); Rh1–Cl1, 2.433(2); Rh1–N1, 2.196(5); Rh1–N2, 2.136(4); Rh1–P1, 2.233(2); Rh1–P2, 2.249(1); P1–O1, 1.570(4); P2–O2, 1.574(5); O1–B1, 1.465(8); O2–B1, 1.479(9); F1–B1, 1.394(8); F2–B1, 1.378(8); P1–Rh1–Cl1, 170.88(6), P1–Rh1–P2, 89.58(6); F2–B1–F1, 110.1(5), O1–B1–O2, 111.9(5), F2–B1–O1, 108.6(5), F1–B1–O2, 109.9(5).

Synthesis of alkyl complexes

The formation of the hydrido-phosphinito rhodium(III) complexes **1** occurs with displacement of 1,5-cyclooctadiene, present in the starting material. Very recently, the reaction of $[Rh(C_2H_4)_2Tp]$ with $PPh_2(O)H$ has been reported to afford a mixture of hydrido-phosphinito and ethyl-phosphinito rhodium (III) derivatives.[19] We thought interesting to study the reactivity of the norbornadiene (nbd) complex $[Rh(\mu\text{-}Cl)(nbd)]_2$ with $PPh_2(O)H$ because rhodium(I) coordinated norbornadiene is well known to insert into Rh(III)–H bonds formed by X–H oxidative addition (X=C, N, B) on $[Rh(\mu\text{-}Cl)(nbd)]_2$ to selectively afford norbornenyl or nortricyclyl derivatives, both in the absence or presence of N- or P-donor ligands.[31]

The reaction of $[Rh(\mu\text{-}Cl)(nbd)]_2$ with 4 equivalents of diphenylphosphine oxide in $CHCl_3$ afforded the neutral dimer unsaturated complex $[Rh(\mu\text{-}Cl)\{(PPh_2O)_2H\}(ntyl)]_2$ (**4**) (ntyl = C_7H_9, nortricyclyl), extremely insoluble in most solvents, shown in Scheme 5. Presumably complex **4** is formed by oxidative addition of a SPO to rhodium assisted by the formation of the coordinated quasi-chelate fragment PO···HOP, subsequent insertion of norbornadiene into the formed Rh–H bond to afford a coordinated σ-norbornenyl and double bond shift with ring closure of the norbornenyl ligand to give the thermodynamically favoured nortricyclyl ligand.[32] Experimental evidence supporting this path could be obtained by following the reaction of $[Rh(\mu\text{-}Cl)(nbd)]_2$ with only 2 equivalents of diphenylphosphine oxide in $CDCl_3$ by NMR that allowed identification of dinuclear mixed-valent Rh(I)/Rh(III) complexes. Sequential oxidative addition of Si–H to $[Rh(\mu\text{-}Cl)(cod)]_2$ has been reported to afford dinuclear mixed-valent Rh(I)/Rh(III) intermediates and final dinuclear Rh(III) species.[33] In the present case, at initial reaction times the formation of $[(nbd)Rh(\mu\text{-}Cl)_2Rh\{(PPh_2O)_2H\}(\sigma\text{-nbyl})]$ (**I1**) (nbyl = σ-C_7H_9, norbornenyl) was observed that transformed into $[(nbd)Rh(\mu\text{-}Cl)_2Rh\{(PPh_2O)_2H\}(ntyl)]$ (**I2**), which un-



Scheme 5. Synthesis of complexes **4** and **5**.

fortunately could not be obtained due to decomposition. (see Sup. Info. for more details).

The characterization of **4** was performed in solution by NMR spectroscopy and ESI-MS. The analytical data agree with the proposed stoichiometry. The ^{1}H NMR spectrum at room temperature shows the signals that correspond to the nortricyclyl fragment in the 2.1–0.8 ppm range and the $^{31}P\{^{1}H\}$ NMR spectrum shows four signals, which are doublet of doublets in the 87–82 ppm range, with $J_{Rh\text{-}P} = 151–161$ Hz and $J_{P\text{-}P} = 30$ Hz, due to two non-equivalent phosphorus atom pairs, bonded to the metal centers mutually cis. For **4** ESI-MS shows a molecular ion at m/z = 633.04 that agrees with $[Rh(PPh_2O)_2(ntyl)Cl]^+$ (calc. for $[M/2–H]^+$ 633.87) and suggests five-coordinated rhodium atoms in **4**.

As in our hydrido-phosphinito mononuclear species **1** (vide supra), complex **4** reacts with $BF_3{\cdot}OEt_2$ to afford the dinuclear species **5**, containing the chelating $\{(PPh_2O)_2BF_2\}$ ligand, showing the expected spectroscopic features. The four $^{31}P\{^{1}H\}$ NMR resonances appear in **5** also as doublet of doublets, in the 100–94 ppm range with $J_{Rh\text{-}P} = 156–160$ Hz and $J_{P\text{-}P} = 33$ Hz, at slightly lower field than the parent compound **4**. Determination of the solid-state structure of **5** was also possible using X-ray diffraction (Figure 5).

In the solid state, **5** consists of two rhodium atoms bridged by two chlorine atoms. The geometry around each rhodium atom is pseudo square-planar pyramidal. The apical position is occupied by a nortricyclyl ligand. All the carbon-carbon distances in the nortricyclyl group agree with single bond distances. Two positions of the base of the pyramid are occupied by the bridging chlorido ligands (Cl1 and Cl1′) in trans position to phosphorus atoms (P1 and P2). The bridging Rh–Cl distances (Rh1–Cl1, 2.4630(9); Rh1–Cl1′, 2.4587(8) Å) are slightly longer than that observed in mononuclear complex **3a**. The Rh1···Rh1′ distance of 3.733 Å excludes any significant metal interaction. The last two positions forming the base of the pyramid are occupied by P1 and P2, the sum of the angles involving P1, P2, Cl1 and Cl1′ around the rhodium atom of 357.9 ° agreeing with the proposed structure. The two phosphorus atoms form a new PO–BF_2–OP ligand, which is coordinated as bidentate via the two PPh_2 moieties (Rh1–P1, 2.2174(9); Rh1–P2, 2.2272(11) Å) to form a six-membered ring chelate. The P–O bond distances are equal.

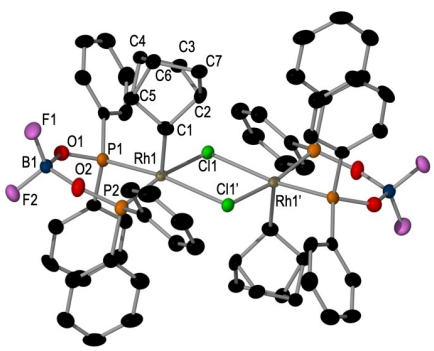
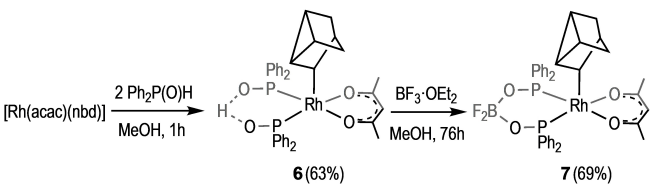


Figure 5. Molecular structure of **5**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°): Rh1–Cl1, 2.4630(9); Rh1–Cl1′, 2.4587(8); Rh1–C1, 2.1116(6); Rh1–P1, 2.2174(9); Rh1–P2, 2.2272(11); P1–O1, 1.560(3); P2–O2, 1.561(2); O1–B1, 1.382(5); O2–B1, 1.465(5); F1–B1, 1.388(4); F2–B1, 1.382(4); P1–Rh1–P2, 87.12(4); P1–Rh1–Cl1, 94.47(3); P2–Rh1–Cl1′, 95.05(3); Cl1–Rh1–Cl1′, 81.33(3); F2–B1–F1, 109.2(3), O1–B1–O2, 113.3(3).

Diphenylphosphine oxide also reacts with [Rh(acac)(nbd)], which undergoes the oxidative addition reaction followed by olefin insertion into the Rh–H bond and C–C bond coupling to afford the five-coordinated nortricyclyl-phosphinito-rhodium(III) derivative with quasi-chelating ligand $[Rh(acac)(ntyl)\{(PPh_2O)_2H\}]$ (**6**) (see Scheme 6). This behavior contrasts with that reported for [Rh(acac)(cod)], where displacement of acetylacetone occurs, to afford a rhodium(I) $[Rh(cod)\{(PPh_2O)_2H\}]$ derivative.[17] Complex **6** also reacts with $BF_3{\cdot}OEt_2$ to give the corresponding $[Rh(acac)(ntyl)\{(PPh_2O)_2BF_2\}]$ (**7**), with chelating diphosphine shown in Scheme 6.

Complexes **6** and **7** have been characterized in solution by NMR spectroscopy. In both complexes the ^{1}H NMR spectra show the expected resonances due to the nortricyclyl and acetylacetonate ligands. In complex **6**, detection of the O···H···O bridge as a singlet at 16.30 ppm requires temperatures lower than 223 K and ^{11}B and ^{19}F NMR confirm the presence of the BF_2 fragment in complex **7**. The $^{31}P\{^{1}H\}$ NMR spectra show two doublets of doublets in both cases, due to non-equivalent phosphorus atoms, with chemical shifts at lower field for complex **7** (96 to 99 ppm range) than for complex **6** (84 to 87 ppm range) and similar $J_{Rh\text{-}P}$ coupling constants (153 and 157 Hz for **6** and **7**, respectively).

X-ray diffraction studies on suitable crystals (Figure 6) confirm the five-coordinated structures shown in Scheme 6. In complexes **6** and **7**, the geometry about the Rh(III) center can be described as a distorted square-planar pyramid with the apical position occupied by C1 of the nortricyclyl ligand (Rh1–C1 2.045(15) Å for **6**; 2.01(2) Å for **7**). The base of the pyramid is occupied by the two phosphorus atoms (P1 and P2) and the acetylacetonate ligand (O3 and O4) in both cases. In compounds **6** and **7**, the rhodium atom being included in the P1P2O3O4 plane, the sum of the four angles (P1–Rh1–P2, P1–Rh1–O4, O4–Rh1–O3 and O3–Rh1–P2) being almost 360° (**6**, 358.3°; **7**, 358.5°) suggests this geometry. In complex **6** the two phosphorus atoms (P1 and P2) form part of a hydrogen bonded quasi-chelate ligand consisting of a phosphinous acid and a phosphinito ligand PO···HOP. The O1···O2 distance of 2.43(2) Å agrees with the existence of a strong hydrogen bond. Both the P–O and also the Rh–P bond distances are equal. On the other hand, the two phosphorus atoms of complex **7** (P1 and P2) form a new P(O)–BF_2–(O)P ligand, as is already the case



Scheme 6. Synthesis of complexes **6** and **7**.

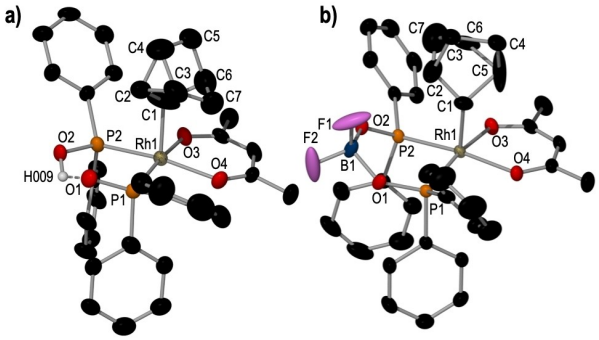


Figure 6. a) Molecular structure of **6**. Displacement ellipsoids are drawn at 50% probability level. Most of hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°): Rh1–O3, 2.098(8); Rh1–O4, 2.809(8); Rh1–P1, 2.248(3); Rh1–P2, 2.250(3); Rh1–C1, 2.045(15); P1–O1, 1.550(9); P2–O2, 1.560(8); O1···(H)O2, 2.43(2); P1–Rh1–P2, 90.8(1); P1–Rh1–O4, 92.1(2); P2–Rh1–O3, 87.9(3); O3–Rh1–O4, 87.5(3); b) Molecular structure of **7**. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms and crystallization solvent molecules have been omitted by clarity. Selected bond lengths (Å) and angles (°): Rh1–C1, 2.01(2); Rh1–P1, 2.2214(8); Rh1–P2, 2.2318(8); P1–O1, 1.5659(17); P2–O2, 1.5687(17); O1–B1, 1.455(3); O2–B1, 1.476(3); F1–B1, 1.375(4); F2–B1, 1.349(4); P1–Rh1–P2, 86.07(3); P1–Rh1–O4, 91.30(5); P2–Rh1–O3, 93.33(5); O3–Rh1–O4, 87.77(7); F2–B1–F1, 108.9(3), O1–B1–O2, 113.1(2).

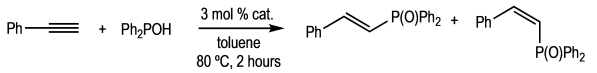
for compounds **3a** and **5**. This new ligand is coordinated to the metal center as bidentate via the two PPh_2 moieties (Rh1–P1 2.2214(8) Å and 2.2318(8) Å) to form a six-membered ring chelate. The P–O bond distances, with values in between the typical range of a single and a double bond, are equally long in **7**, P1–O1, 1.5659(17) Å and P2–O2, 1.5687(17) Å. Exchange of O···H···O by O–BF_2–O is reflected in a smaller P–Rh–P bite angle, as observed in related rhodium(I) [Rh(cod){$(PPh_2O)_2X$}] (X=H or BF_2) derivatives.[17]

Hydrophosphinylation of phenylacetylene

We have studied the behavior of our diphenylphosphine oxide Rh(III) derivatives, including hydrido-phosphinous acid-phosphinito-rhodium(III) complexes, as precatalysts in the hydrophosphinylation of phenylacetylene. Hydrido-phosphinito-rhodium (III) complexes have been proposed as intermediates in hydrophosphinylation of alkynes using SPOs catalyzed by rhodium(I) complexes.[10, 11a] These reactions are less efficient when using phenylacetylenes than when using alkylacetylenes. Phenylacetylenes may undergo competitive polymerization reactions more easily.[11a, 34] Our catalytic experiments were carried out under previously reported reaction conditions,[10, 11a] using 3 mol% of precatalyst (1.5 mol% when using complex **4**) in toluene at 80 °C and the results have been included in Table 1.

Regarding the bipy and Me_2-bipy rhodium complexes **1a**–**1d**, we find that while rhodium(III) complexes **1a**–**1c** are unable to catalyze the hydrophosphinylation reaction (Table 1, entries 1–3), complex **1d** reached complete conversion with a 100% selectivity for the (*E*)-diphenyl(styryl)phosphine oxide (Table 1, entry 4). This fact suggests that in these complexes the steric hindrance provided by the coordinated N-donor ligand in **1d** is required for the hydrophosphinylation reaction to occur. In a similar fashion, when using 1,10-phenanthroline complexes **1e**-**1h**, the catalytic results are in accordance with those obtained for the **1a**–**1d** complexes. Rhodium(III) complexes with encumbered 2,9-Me_2-phen ligands, compounds **1e** and **1f**, are able to catalyse the hydrophosphinylation of phenylacetylene with a conversion of 74% when **1e** is used as precatalyst (Table 1, entry 5) and 93% when **1f** is used (Table 1, entry 6). When using these complexes as precatalysts a high selectivity for the formation of the (*E*)-diphenyl(styryl)phosphine oxide, 85% or 90% for **1e** or **1f** respectively, is obtained (Table 1, entries 5 and 6). On the other hand, complexes **1g** and **1h** are ineffective as pre-catalysts of the studied reaction (Table 1, entries 7 and 8).

Table 1. Hydrophosphinylation of phenylacetylene.[a]



Entry	Catalyst	Conv. [%][b]	trans:cis
1	**1a**	–	–
2	**1b**	–	–
3	**1c**	–	–
4	**1d**	100	100:0
5	**1e**	74	85:15
6	**1f**	93	90:10
7	**1g**	–	–
8	**1h**	–	–
9	**2a**	–	–
10	**3e**	4	100:0
11	**4**	55	100:0
12	**6**	–	–

[a] Reaction conditions: phenylacetylene (0.074 mmol) and $Ph_2P(O)H$ (0.074 mmol) with 3 mol% of [Rh] (0.0022 mmol) in 1 mL of toluene at 80 °C. [b] Conversions determined by ^1H NMR using dichloroethane as internal standard (added at the end of the reaction). [c] Trans/cis ratio determined by ^1H NMR.

The results obtained when using complexes **1** thus indicate that those hydrido complexes unable to undergo the hydride/chloride exchange are effective catalysts, while those complexes undergoing the hydride/chloride exchange are ineffective as catalysts. This correlation suggests that, as previously proposed, hydrido rhodium derivatives are required intermediates. According to this, complex **2a** of the dichloride type is unable to catalyze this reaction (Table 1, entry 9). These results prompt us to conclude that, most likely, complexes containing diimine ligands with lower steric hindrance (compounds **1a**, **1b**, **1c**, **1g** and **1h**) undergo, under our reaction conditions, a deactivation of the catalyst that can be related to loss of hydride due to hydride/chloride exchange. Bidentate N-donors such as ethylenediamine have been used as auxiliary ligands to promote the hydrophosphinylation of phenylacetylene with $PPh_2(O)H$ using CuI (10 mol%) in DMSO at 60 °C. (E)-diphenyl(styryl)phosphine oxide was obtained with >90% yield and >95% regio- and stereoselectivity.[13] High yields and selectivities were also obtained at room temperature using [$Ni(PPh_2Me)_4$] (0.5 mol%) in EtOH[12] or [$RhBr(PPh_3)_3$] (3 mol%) in toluene,[10] or at 70 °C using [$Pd(PPh_3)_4$] (5 mol%) in benzene.[9]

Finally, we tested a complex containing the chelating Ph_2PO-BF_2-$OPPh_2$ ligand. The 2,9-Me_2-phen complex **3 e** exhibits a very low catalytic activity (4%) towards the hydrophosphinylation of phenylacetylene (Table 1, entry 10) showing that exchange of the hydrogen bond in the quasi-chelate $Ph_2PO\cdots H\text{–}OPPh_2$ by BF_2 drastically inhibits the catalytic activity. This may be due, among others, to the acidic proton sited in the quasi-chelate derivative playing an important role in the reaction mechanism and/or to the requirement of a coordination vacancy, which could be easier for the quasi-chelate complex than for the chelate complex.

Related to the requirement of coordination vacancies in the precatalyst, coordinatively unsaturated nortricyclyl-diphenylphosphinous acid-phosphinito containing complexes **4** and **6** have also been tested in the hydrophosphinylation of phenylacetylene. Complex **4**, an alkyl-chloride derivative, catalyzes this reaction with a 100% selectivity for the (*E*)-diphenyl(styryl) phosphine oxide (Table 1, entry 11) though with lower activity than the hydrido-chloride-diimine complexes. On the other hand, the alkyl-acetyacetonate derivative **6** is completely inactive under our reaction conditions. Therefore substitution of bridging chlorides by the chelating anionic O-donor inhibits the catalytic reaction. We thus find that the chloride-hydrido-rhodium(III) complexes, stabilized by diimine ligands, appear optimal for the hydrophosphinylation of phenylacetylenes.

Conclusions

Diolefinic rhodium(I) complexes undergo the oxidative addition of SPOs, assisted by the formation of hydrogen bonded phosphinous acid-phosphinito ($Ph_2PO\cdots H\cdots OPPh_2$)-$\kappa^2$P quasi-chelates, to afford hydrido-rhodium(III) complexes. Sterically encumbered diimine ligands stabilize the hydride complexes towards the hydride/chloride exchange. Norbornadiene complexes undergo subsequent olefin insertion into the Rh–H bond and rearrangement to afford nortricyclyl derivatives. The hydrogen bond in the coordinated quasi-chelate exchanges with BF_2 to give bidentate ($Ph_2PO\text{–}BF_2\text{–}OPPh_2$)-$\kappa^2$P. Hydrido-chloride-diimine-rhodium(III) complexes are efficient and regioselective catalysts in the hydrophosphinylation of phenylacetylene with diphenylphosphine oxide to produce (*E*)-diphenyl(styryl) phosphine oxide. The catalytic activity of alkyl-chloride-Rh(III) is lower than that of hydrido-chloride-diimine derivatives. Substitution of the acidic proton in the quasi-chelate by BF_2 and of chloride by acetylacetonate inhibits the catalytic activity.

Experimental Section

The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. Solid compounds were kept in a desiccator containing $CaCl_2$ under air. CH_2Cl_2 was distilled from CaH_2, and THF and toluene were distilled from Na, degassed by successive freeze-pump-thaw cycles and stored over molecular sieves (3 Å). Complexes $[RhCl(cod)]_2$ and $[RhCl(nbd)]_2$[35] were prepared as previously reported. [Rh(acac)(nbd)], diphenylphosphine oxide, bipyridines, phenanthrolines, phenylacetylene and $BF_3{\cdot}OEt_2$ were purchased from Aldrich and used without previous purification. Microanalyses were carried out with a Leco Truspec Micro microanalyzer. IR spectra were recorded with a Nicolet FTIR 510 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. NMR spectra were recorded with Bruker Avance DPX 300, Bruker Avance 400 or Bruker Avance 500 spectrometers at room temperature unless otherwise stated; ^1H and $^{13}C\{^1H\}$ (residual solvent signals), $^{31}P\{^1H\}$ (H_3PO_4 external standard), ^{11}B ($BF_3{\cdot}OEt_2$ external standard) and ^{19}F NMR (CF_3COOH external standard) spectra were measured from $CDCl_3$, CD_2Cl_2, or DMSO-d_6 solutions. ESI-MS were recorded on a Bruker MicrOTOF-Q instrument. In all ESI-MS spectra there was a good fit to both the principal molecular ion and the overall isotopic distribution.

Preparation of complexes 1 a–1 d. To a Schlenk charged with $[RhCl(cod)]_2$ (50 mg, 0.101 mmol) in THF (5 mL), 2 equivalents of bipyridine (2,2′-bipyridine, 32 mg, 0.202 mmol; 4,4′-Me_2-2,2′-bipyridine, 37.5 mg, 0.202 mmol; 5,5′-Me_2-2,2′-bipyridine, 37.5 mg, 0.202 mmol; 6,6′-Me_2-2,2′-bipyridine, 37.5 mg, 0.202 mmol) were added and stirred for 15 minutes. After this time, 4 equivalents of diphenylphosphine oxide (82 mg, 0.404 mmol) were added to this mixture. The mixture was stirred for 1 hour and a white solid is formed. This white solid is extracted from the reaction mixture and dried under vacuum. Yield of **1 a** 130 mg (92%). Yield of **1 b** 115 mg (78%). Yield of **1 c** 102 mg (69%). Yield of **1 d** 100 mg (80%).

1 a: ^1H NMR (400 MHz, DMSO-d_6): δ 8.93–6.32 (28 $H_{aromatics}$), −13.96 (dt, $J_{P\text{-}H}=33$, $J_{Rh\text{-}H}=J_{P\text{-}H}=17$ Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 96.6 (dd, $J_{Rh\text{-}P}=134$ Hz, $J_{P\text{-}P}=31$ Hz), 90.0 (dd, $J_{Rh\text{-}P}=127$ Hz, $J_{P\text{-}P}=31$ Hz). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 155.0–123.7 (34 $C_{aromatics}$). Microanalysis ($RhC_{34}H_{30}N_2P_2O_2Cl$) Requires: C 58.43, H 4.33, N 4.01. Obtained: C 58.05, H 4.59, N 4.21. ESI-MS (CH_3CN): calc. for $[Rh(H)(PPh_2OH)(PPh_2O)(2,2'\text{-bipy})]^+$, $[M-Cl]^+$: 663.08. Found: 663.08. IR (KBr, cm^{-1}): 2081 (s), ν(Rh–H); 1097 (s), ν(P–O)/ν(P=O).

1 b: ^1H NMR (400 MHz, CD_2Cl_2): δ 8.54–6.45 (26 $H_{aromatics}$), 2.36 (s, 3H, CH_3 bipy), 2.25 (s, 3H, CH_3 bipy), −13.90 (dt, $J_{P\text{-}H}=33$, $J_{Rh\text{-}H}=J_{P\text{-}H}=17$ Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 97.2 (dd, $J_{Rh\text{-}P}=135$ Hz, $J_{P\text{-}P}=31$ Hz), 92.6 (dd, $J_{Rh\text{-}P}=128$ Hz, $J_{P\text{-}P}$ 31 Hz). Microanalysis ($RhC_{36}H_{34}N_2P_2O_2Cl$): Requires: C 59.48, H 4.71, N 3.85. Obtained: C 59.23, H 4.58, N 3.55. ESI-MS (CH_3CN): calc. for $[RhH(PPh_2OH)(PPh_2O)(4,4'\text{-}Me_2\text{-}2,2'\text{-bipy})]^+$, $[M-Cl]^+$: 691.53. Found: 691.11. IR (KBr, cm^{-1}): 2115 (s), ν(Rh–H); 1098 (s), ν(P–O)/ν(P=O).

1 c: ^1H NMR (400 MHz, CD_2Cl_2): δ 8.45–6.65 (26 $H_{aromatics}$), 2.23 (s, 3H, CH_3 bipy), 1.82 (s, 3H, CH_3 bipy), −14.12 (dt, $J_{P\text{-}H}=33$, $J_{Rh\text{-}H}=J_{P\text{-}H}=17$ Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 95.3 (dd, $J_{Rh\text{-}P}=134$ Hz, $J_{P\text{-}P}=29$ Hz), 92.1 (dd, $J_{Rh\text{-}P}=127$ Hz, $J_{P\text{-}P}=29$ Hz). Microanalysis ($RhC_{36}H_{34}N_2P_2O_2Cl$): Requires: C 59.48, H 4.71, N 3.85. Obtained: C 59.01, H 4.65, N 3.43. IR (KBr, cm^{-1}): 2059 (s), ν(Rh–H); 1096 (s), ν(P–O)/ν(P=O).

1d: ^1H NMR (400 MHz, CD_2Cl_2): δ 8.26–6.65 (26 $H_{aromatics}$), 2.65 (s, 3H, CH_3 bipy), 2.56 (s, 3H, CH_3 bipy), −14.51 (dt, $J_{P\text{-}H}=33$, $J_{Rh\text{-}H}=J_{P\text{-}H}=17$ Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 95.1 (dd, $J_{Rh\text{-}P}=134$ Hz, $J_{P\text{-}P}=32$ Hz), 77.9 (dd, $J_{Rh\text{-}P}=130$ Hz, $J_{P\text{-}P}=32$ Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.2-120.8 (34 $C_{aromatics}$), 30.6 (s, CH_3 bipy), 29.0 (d, $J=4$ Hz, CH_3 bipy). Microanalysis ($RhC_{36}H_{34}N_2P_2O_2Cl$): Requires: C 59.48, H 4.71, N 3.85. Obtained C 59.19, H 4.47, N 3.71. IR (KBr, cm^{-1}): 2195 (s), ν(Rh–H); 1094 (s), ν(P–O)/ν(P=O).

Preparation of complexes 1 e–1 h. To a Schlenk charged with $[RhCl(cod)]_2$ (20 mg, 0.041 mmol), 2 equivalents of phenanthroline (2,9-Me_2-1,10-phenanthroline, 17 mg, 0.081 mmol; 2,9-Me_2-4,7-Ph_2-1,10-phenanthroline, 29 mg, 0.081 mmol; 5,6-Me_2-1,10-phenanthroline, 17 mg, 0.081 mmol; 4,7-Ph_2-1,10-phenanthroline, 27 mg, 0.081 mmol) and 4 equivalents of diphenylphosphine oxide (33 mg, 0.162 mmol), 5 mL of CH_2Cl_2 were added. The yellow solution

formed was stirred for 24 hour and concentrated under vacuum. Addition of 20 mL of pentane gave a yellow precipitate that was dried under vacuum. Yield of **1 e** 40 mg (66%). Yield of **1 f** 47 mg (65%). Yield of **1 g** 53 mg (87%). Yield of **1 h** 56 mg (80%).

1 e: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.37–6.34 (32 $H_{aromatics}$), 2.96 (s, 3H, CH_3 phen), 2.82 (s, 3H, CH_3 phen), −14.11 (dt, $J_{P\text{-}H}$ = 38 Hz, $J_{Rh\text{-}H}$ = $J_{P\text{-}H}$ = 15 Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 96.0 (dd, $J_{Rh\text{-}P}$ = 133 Hz, $J_{P\text{-}P}$ = 33 Hz), 78.1 (dd, $J_{Rh\text{-}P}$ = 130 Hz, $J_{P\text{-}P}$ = 33 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 163.0–126.0 (36 $C_{aromatics}$), 31.4 (d, J = 2 Hz, CH_3 phen), 30.0 (d, J = 4 Hz, CH_3 phen). Microanalysis ($RhC_{38}H_{34}N_2P_2O_2Cl \cdot 0.5CH_2Cl_2$): Requires: C 58.28, H 4.45, N 3.53. Obtained: C 58.64, H 4.40, N 3.46. ESI-MS (CH_3CN): calc. for [RhH(PPh_2OH)(PPh_2O)(2,9-Me_2-1,10-phen)]$^+$, [M−Cl]$^+$: 715.55. Found: 715.11. IR (KBr, cm^{-1}): 2166 (s), ν(Rh–H); 1098 (s), ν(P–O)/ν(P=O).

1 f: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.40–6.40 (40 $H_{aromatics}$), 3.11 (s, 3H, CH_3 phen), 2.95 (s, 3H, CH_3 phen), −13.85 (dt, $J_{P\text{-}H}$ = 38 Hz, $J_{Rh\text{-}H}$ = $J_{P\text{-}H}$ = 13 Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 92.5 (dd, $J_{Rh\text{-}P}$ = 132 Hz, $J_{P\text{-}P}$ = 34 Hz), 72.0 (dd, $J_{Rh\text{-}P}$ = 129 Hz, $J_{P\text{-}P}$ = 34 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 162.3–123.5 (48 $C_{aromatics}$), 31.9 (s, CH_3 phen), 30.4 (d, J = 5 Hz, CH_3 phen). Microanalysis ($RhC_{50}H_{42}N_2P_2O_2Cl$): Requires: C 66.49, H 4.69, N 3.10. Obtained: C 66.44, H 4.68, N 3.25. ESI-MS (CH_3CN): calc. for [RhH(PPh_2OH)(PPh_2O)(2,9-Me_2-4,7-Ph_2-1,10-phen)]$^+$, [M−Cl]$^+$: 867.75. Found: 867.17. IR (KBr, cm^{-1}): 2138 (s), ν(Rh–H); 1097 (s), ν(P–O)/ν(P=O).

1 g: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.08–6.12 (26 $H_{aromatics}$), 2.65 (s, 3H, CH_3 phen), 2.62 (s, 3H, CH_3 phen), −13.67 (dt, $J_{P\text{-}H}$ = 32 Hz, $J_{Rh\text{-}H}$ = $J_{P\text{-}H}$ = 17 Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 97.5 (dd, $J_{Rh\text{-}P}$ = 134 Hz, $J_{P\text{-}P}$ = 31 Hz), 91.3 (dd, $J_{Rh\text{-}P}$ = 127 Hz, $J_{P\text{-}P}$ = 31 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 153.0–124.2 (36 $C_{aromatics}$), 15.5 (s, CH_3 phen), 15.4 (s, CH_3 phen). Microanalysis ($RhC_{38}H_{34}N_2P_2O_2Cl$): Required: C 60.77, H 4.56, N 3.73. Obtained: C 60.81, H 4.46, N 3.48. ESI-MS (CH_3CN): calc. for [RhNa(PPh_2OH)(PPh_2O)(5,6-Me_2-1,10-phen)]$^+$, [M−Cl]$^+$: 737.54. Found: 737.10. IR (KBr, cm^{-1}): 2091 (s), ν(Rh–H); 1098 (s), ν(P–O)/ν(P=O).

1 h: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.30–6.17 (36 $H_{aromatics}$), −13.47 (dt, $J_{P\text{-}H}$ = 32 Hz, $J_{Rh\text{-}H}$ = $J_{P\text{-}H}$ = 16 Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 98.1 (dd, $J_{Rh\text{-}P}$ = 134 Hz, $J_{P\text{-}P}$ = 31 Hz), 91.3 (dd, $J_{Rh\text{-}P}$ = 127 Hz, $J_{P\text{-}P}$ = 31 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 153.9–125.2 (48 $C_{aromatics}$). Microanalysis ($RhC_{48}H_{38}N_2P_2O_2Cl$): Requires: C 65.88, H 4.38, N 3.20. Obtained: C 65.54, H 4.27, N 3.13. ESI-MS (CH_3CN): calc. for [RhH(PPh_2OH)(PPh_2O)(4,7-Ph_2-1,10-phen)]$^+$, [M−Cl]$^+$: 839.70. Found: 839.15. IR (KBr, cm^{-1}): 2076 (s), ν(Rh–H); 1098 (s), ν(P–O)/ν(P=O).

Preparation of complexes 2 a-2 c. To a Schlenk charged with the hydrido-phosphinite-Rh(III) complex (**1 a**, 25 mg, 0.036 mmol; **1 b**, 25 mg, 0.034 mmol; **1 c**, 25 mg, 0.034 mmol) 5 mL of CH_2Cl_2 was added. After 3 days stirring, the orange solution formed was concentrated under vacuum. Addition of 20 mL of Et_2O gave a pale-yellow precipitate that was extracted and dried under vacuum. Yield of **2 a** 23 mg (86%). Yield of **2 b** 22 mg (85%). Yield of **2 c** 20 mg (77%).

2 a: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.30–6.47 (28 $H_{aromatics}$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 73.5 (dd, $J_{Rh\text{-}P}$ = 118 Hz, $J_{P\text{-}P}$ = 23 Hz), 69.0 (dd, $J_{Rh\text{-}P}$ = 111 Hz, $J_{P\text{-}P}$ = 23 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 155.0–122.9 (34 $C_{aromatics}$). Microanalysis ($RhC_{34}H_{29}N_2P_2O_2Cl_2$): Required: C 55.68, H 3.99, N 3.82. Obtained: C 55.32, H 3.85, N 3.86. ESI-MS (CH_3CN): calc. for [RhCl(PPh_2OH)(PPh_2O)(2,2′-bipy)]$^+$, [M−Cl]$^+$: 697.04. Found: 697.05. IR (KBr, cm^{-1}): 1097 (s), ν(P–O)/ν(P=O).

2 b: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19–6.24 (26 $H_{aromatics}$), 2.54 (s, 3H, CH_3 bipy), 2.29 (s, 3H, CH_3 bipy). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 74.9 (dd, $J_{Rh\text{-}P}$ = 117 Hz, $J_{P\text{-}P}$ = 23 Hz), 69.2 (dd, $J_{Rh\text{-}P}$ = 110 Hz, $J_{P\text{-}P}$ 23 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 154.4-123.7 (34 $C_{aromatics}$), 22.0 (s, CH_3 bipy), 21.3 (s, CH_3 bipy). Microanalysis ($RhC_{36}H_{33}N_2P_2O_2Cl_2$): Requires: C 56.79, H 4.37 N 3.68. Obtained: C 56.19, H 4.23, N 3.88. IR (KBr, cm^{-1}): 1097 (s), ν(P–O)/ν(P=O).

2 c: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.82-6.84 (26 $H_{aromatics}$), 2.36 (s, 3H, CH_3 bipy), 1.42 (s, 3H, CH_3 bipy). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 71.9 (dd, $J_{Rh\text{-}P}$ = 117 Hz, $J_{P\text{-}P}$ = 23 Hz), 68.4 (dd, $J_{Rh\text{-}P}$ = 110 Hz, $J_{P\text{-}P}$ = 23 Hz). Microanalysis ($RhC_{36}H_{33}N_2P_2O_2Cl_2 \cdot 0.5CH_2Cl_2$): Requires: C 54.53, H 4.26, N 3.48. Found: C 54.48, H 4.21, N 3.01. ESI-MS (CH_3CN): calc. for [RhCl(PPh_2OH)(PPh_2O)(5,5′-Me_2-2,2′-bipy)]$^+$, [M−Cl]$^+$: 725.97. Found: 725.10. IR (KBr, cm^{-1}): 1096 (s), ν(P–O)/ν(P=O).

Preparation of complexes 2 g and 2 h. To a Schlenk charged with the hydrido-phosphinite-Rh(III) complex (**1 g**, 30 mg, 0.040 mmol; **1 h**, 30 mg, 0.034 mmol) 5 mL of $CHCl_3$ was added. After 7 days stirring, a pale-yellow solid is formed, which was dried under vacuum. Yield of **2 g** 28 mg (89%). Yield of **2 h** 25 mg (81%).

2 g: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.53-6.52 (26 $H_{aromatics}$), 2.79 (s, 3H, CH_3 phen), 2.68 (s, 3H, CH_3 phen). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 74.0 (dd, $J_{Rh\text{-}P}$ = 117 Hz, $J_{P\text{-}P}$ = 23 Hz), 69.2 (dd, $J_{Rh\text{-}P}$ = 109 Hz, $J_{P\text{-}P}$ = 23 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 153.7-124.4 (36 $C_{aromatics}$), 15.7 (s, CH_3 phen), 15.6 (s, CH_3 phen). Microanalysis ($RhC_{38}H_{33}N_2P_2O_2Cl_2 \cdot 0.25CHCl_3$): Requires: C 56.34, H 4.11, N 3.44. Obtained: C 55.81, H 3.90, N 3.61. ESI-MS (CH_3CN): calc. for [RhCl(PPh_2OH)(PPh_2O)(5,6-Me_2-1,10-phen)]$^+$, [M−Cl]$^+$: 749.99. Found: 749.99. IR (KBr, cm^{-1}): 1095 (s), ν(P–O)/ν(P=O).

2 h: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.80 (t, $J_{H\text{-}H}$ = 5 Hz, CH=N), 7.97 (d, $J_{H\text{-}H}$ = 5 Hz, CH=N), 8.58–6.54 (34 $H_{aromatics}$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 74.9 (dd, $J_{Rh\text{-}P}$ = 117 Hz, $J_{P\text{-}P}$ = 23 Hz), 69.4 (dd, $J_{Rh\text{-}P}$ = 109 Hz, $J_{P\text{-}P}$ = 23 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 154.4-125.4 (48 $C_{aromatics}$). Microanalysis ($RhC_{48}H_{37}N_2P_2O_2Cl_2$): Requires: C 63.38, H 4.10, N 3.08. Obtained: C 62.94, H 4.29, N 3.19. ESI-MS (CH_3CN): calc. for [RhCl(PPh_2OH)(PPh_2O)(4,7-Ph_2-1,10-phen)]$^+$, [M−Cl]$^+$: 873.14. Found: 873.11. IR (KBr, cm^{-1}): 1096 (s), ν(P–O)/ν(P=O).

Preparation of complexes 3 a and 3 e. To a Schlenk charged with **1 a** (40 mg, 0.057 mmol) or **1 e** (30 mg, 0.040 mmol) and 3 mL of THF or CH_2Cl_2, an excess of $BF_3 \cdot OEt_2$ (18 μL, 0.143 mmol or 15 μL, 0.119 mmol) was added. After 16 hours stirring, a new white solid is formed. This new white solid is extracted and dried under vacuum. Yield of **3 a** 42 mg (98%) or **3 e** 27 mg (85%).

3 a: ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.07-6.31 (28 $H_{aromatics}$), −13.58 (dt, $J_{P\text{-}H}$ = 33 Hz, $J_{Rh\text{-}H}$ = $J_{P\text{-}H}$ = 16 Hz, 1H, Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 109.0 (dd, $J_{Rh\text{-}P}$ = 139 Hz, $J_{P\text{-}P}$ 32 Hz), 98.3 (dd, $J_{Rh\text{-}P}$ = 126 Hz, $J_{P\text{-}P}$ = 32 Hz). ^{11}B NMR (128 MHz, DMSO-d_6): δ 1.1 (s, br). ^{19}F NMR (376 MHz, DMSO-d_6): δ −131.1 (d, $J_{F\text{-}F}$ = 69 Hz), −133.9 (d, $J_{F\text{-}F}$ = 70 Hz). Microanalysis ($RhC_{34}H_{29}N_2P_2O_2BF_2Cl$): Requires: C 54.69, H 3.91, N 3.75. Obtained: C 54.36, H 3.87, N 3.76. ESI-MS (CH_3CN): calc. for [Rh(bipy)(H)Na{($PPh_2O)_2BF_2$}]$^+$, [M−Cl]$^+$: 733.26. Found: 733.06. IR (KBr, cm^{-1}): 2104 (s), ν(Rh–H); 1103 (s) and 1052 (m), ν(B–F); 1011 (s), ν(P–O); 898 (m), ν(O–B-O).

3 e: ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.52-6.19 (26 $H_{aromatics}$), 2.88 (s, 3H, CH_3 phen), 2.53 (s, 3H, CH_3 phen), −14.79 (dt, $J_{P\text{-}H}$ = 39 Hz, $J_{Rh\text{-}H}$ = $J_{P\text{-}H}$ = 17 Hz, 1H Rh–H). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ 108.4 (dd, $J_{Rh\text{-}P}$ = 137 Hz, $J_{P\text{-}P}$ = 36 Hz), 84.6 (dd, $J_{Rh\text{-}P}$ = 129 Hz, $J_{P\text{-}P}$ = 35 Hz). ^{11}B NMR (128 MHz, DMSO-d_6): δ 0.97 (s, br). ^{19}F NMR (376 MHz, DMSO-d_6): δ −132.0 (d, $J_{F\text{-}F}$ = 71 Hz), −133.1 (d, $J_{F\text{-}F}$ = 72 Hz). Microanalysis ($RhC_{38}H_{33}N_2P_2O_2ClBF_2 \cdot 0.5CH_2Cl_2$): Requires: C 54.97, H 4.07, N 3.33. Obtained: C 54.91, H 4.10, N 2.82. IR (KBr, cm^{-1}): 2213 (s), ν(Rh–H); 1101 (s) and 1061 (m), ν(B–F); 1012 (s), ν(P–O); 896 (m), ν(O–B-O).

Preparation of complex 4. A solution of complex $[RhCl(nbd)]_2$ (20 mg, 0.043 mmol) in 2 mL chloroform was cooled in an ice/salt bath and a solution of $PPh_2(O)H$ (42 mg, 0.20 mmol) in 1 mL $CHCl_3$ was added dropwise under stirring. Allowing the bath reaching

room temperature and stirring for 16 hours afforded a yellow precipitate that was filtered off, washed with diethyl ether and dried under vacuum. Yield of **4** 35 mg (64%).

4: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.14-6.94 (40 $H_{aromatics}$), 3.71 (d, J = 6.0 Hz, 1 H), 2.02 (d, J = 19.6 Hz, 2H), 1.50 (m, 2H), 1.38 (s, 1H), 1.15 (m, 2H), 0.89 (s, 1H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 86.8 (dd, J_{Rh-P} = 151 Hz, J_{P-P} = 30 Hz), 86.7 (dd, J_{Rh-P} = 152 Hz, J_{P-P} = 30 Hz), 82.7 (dd, J_{Rh-P} = 161 Hz, J_{P-P} = 29 Hz), 82.6 (dd, J_{Rh-P} = 161 Hz, J_{P-P} = 30 Hz). Microanalysis ($Rh_2C_{62}H_{60}Cl_2P_4O_4$): Requires: C 58.65, H 4.76. Obtained: C 58.54, H 4.81. ESI-MS (CH_3CN): calc. for [Rh(Cl)(ntyl)(PPh_2O)(PPh_2O)]$^+$, [M/2-H]$^+$: 633.87. Found: 633.04. IR (KBr, cm^{-1}): 1097 (s), ν(P–O)/ν(P=O).

Preparation of complex 5. To a suspension of complex [Rh(μ-Cl)(ntyl)(PPh_2OH)(PPh_2O)]$_2$ (**4**) (20 mg, 0.016 mmol) in 3 mL chloroform $BF_3 \cdot OEt_2$ (4.9 μL, 0.039 mmol) was added. The resultant yellow solution was stirred for 16 hours to afford a precipitate that was filtered off, washed with diethyl ether and dried under vacuum. Yield of **5** 10 mg (47%).

5: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.14–6.94 (40 $H_{aromatics}$), 4.01 (s, 1H), 1.98 (t, J = 11.7 Hz, 2H), 1.67 (d, J = 4.8 Hz, 2H), 1.57 (s, 1H), 1.50 (s, 1H), 1.38 (s, 1H), 1.17 (t, J = 8.7 Hz, 1H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 99.2 (dd, J_{Rh-P} = 157 Hz, J_{P-P} = 32 Hz), 98.7 (dd, J_{Rh-P} = 156 Hz, J_{P-P} = 33 Hz), 95.3 (dd, J_{Rh-P} = 162 Hz, J_{P-P} = 33 Hz), 94.7 (dd, J_{Rh-P} = 160 Hz, J_{P-P} = 33 Hz). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 135.2–128.0 (48 $C_{aromatics}$), 70.4 (d, J_{Rh-C} = 28 Hz, 1 C), 41.3 (1 C), 34.7 (1 C), 33.1 (1 C), 21.5 (1 C), 17.9 (1 C), 17.1 (1 C). ^{11}B NMR (128 MHz, CD_2Cl_2): δ 1.0 (s, br). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −132.6 (d, J_{F-F} = 74 Hz), −138.2 (d, J_{F-F} = 74 Hz). Microanalysis ($Rh_2C_{62}H_{58}B_2Cl_2F_4P_4O_4 \cdot 0.5CHCl_3$): Requires: C 52.68, H 4.14. Obtained: C 52.94, H 4.15. IR (KBr, cm^{-1}): 1102 (s) and 1049 (m), ν(B–F); 1015 (s), ν(P–O); 876 (m), ν(O–B-O).

Preparation of complex 6. To a suspension of [Rh(acac)(nbd)] (30 mg, 0.102 mmol) in 2 mL methanol, $PPh_2(O)H$ (41 mg, 0.204 mmol) was added to afford a solution. After 1 hour stirring a yellow solid was formed that was filtered off, washed with diethyl ether and dried under vacuum. Yield of **6** 45 mg (63%).

6: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20–7.13 (20 $H_{aromatics}$), 5.71 (s, 1H, HC_{acac}), 3.31 (t, J = 5.5 Hz, 1H), 2.16 (s, 6 H, CH_3), 1.31 (s, 1H), 1.15 (m, 2H), 0.95 (t, J = 5.2 Hz, 1H), 0.91 (t, J = 5.2 Hz, 1H), 0.83 (d, J = 9.6 Hz, 1H), 0.78 (d, J = 5.1 Hz, 1H), 0.66 (d, J = 10.4 Hz, 1H). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 86.7 (dd, J_{Rh-P} = 153 Hz, J_{P-P} = 47 Hz), 84.2 (dd, J_{Rh-P} = 154 Hz, J_{P-P} = 47 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 187.4 (O = C_{acac}), 132.0–127.9 ($C_{aromatics}$), 100.2 (HC_{acac}), 56.8 (dt, J_{Rh-C} = 31 Hz, J_{P-C} = 6 Hz, 1 C), 37.2 (1 C), 32.5 (1 C), 31.9 (1 C), 27.8 (2 CH_3), 19.7 (1 C), 15.0 (1 C), 14.6 (1 C). Microanalysis ($RhC_{36}H_{37}P_2O_4$): Requires: C 61.90, H 5.34, Obtained: C 62.07, H 4.99. ESI-MS (CH_3OH): calc. for [Rh(acac)(ntyl)(PPh_2OH)(PPh_2O)H]$^+$, [M + H]$^+$: 699.55. Found: 699.13. IR (KBr, cm^{-1}): 1577 (s) and 1516 (s), ν(C=O); 1098 (s), ν(P–O)/ν(P=O).

Preparation of complex 7. To a suspension of complex [Rh(acac)(ntyl)(PPh_2OH)(PPh_2O)] (**6**) (35 mg, 0.05 mmol) in 3 mL methanol $BF_3 \cdot OEt_2$ (15.5 μL, 0.125 mmol) was added. After 3 days stirring the yellow solid was filtered off, washed with diethyl ether and dried under vacuum. Yield of **7** 26 mg (69%).

7: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35–6.87 (20 $H_{aromatics}$), 5.68 (s, 1H, HC_{acac}), 3.63 (t, J = 5.5 Hz, 1H), 2.15 (s, 6 H, CH_3), 1.43 (s, 1H), 1.23 (d, J = 9.8 Hz, 1H), 1.03 (s, 1H), 1.01 (s, 1H), 0.93 (s, 1H), 0.79 (d, J = 9.6, 2H), 0.63 (d, J = 10.3 Hz, 1H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 98.5 (dd, J_{Rh-P} = 156 Hz, J_{P-P} = 53 Hz), 96.9 (dd, J_{Rh-P} = 158 Hz, J_{P-P} = 53 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 188.1 (O=C_{acac}), 138.4-126.1 (48 $C_{aromatics}$), 101.5 (HC_{acac}), 63.3 (d, J_{Rh-C} = 31 Hz, 1 C), 38.2 (1 C), 33.2 (1 C), 32.7 (1 C), 28.7 (2 CH_3) 20.3 (1 C), 16.9 (1 C), 15.8 (1 C). ^{11}B NMR (128 MHz, $CDCl_3$): δ 1.3 (s, br). ^{19}F NMR (376 MHz, $CDCl_3$): δ −135.2 (d, J_{F-F} = 75 Hz), −137.8 (d, J_{F-F} = 76 Hz). Microanalysis ($RhC_{36}H_{36}BF_2P_2O_4$): Requires: C 57.94, H 4.86. Obtained: C 58.16, H 4.60. IR (KBr, cm^{-1}): 1571 (s) and 1516 (s), ν(C=O);1104 (s) and 1049 (m), ν(B–F); 1010 (s), ν(P–O); 893 (m), ν(O–B-O).

General procedure for the reaction of phenylacetylene with diphenylphosphine oxide. A Schlenk tube was charged with the catalyst (**1 a**, 1.54 mg, 0,0022 mmol; **1 b**, 1.60 mg, 0.0022 mmol; **1 c**, 1.60 mg, 0.0022 mmol; **1 d**, 1.60 mg, 0.0022 mmol, **1 e**, 1.65 mg, 0.0022 mmol, **1 f**, 1.99 mg, 0.0022 mmol, **1 g**, 1.65 mg, 0.0022 mmol, **1 h**, 1.92 mg, 0.0022 mmol; **2 a**,1.63 mg, 0.0022 mmol; **3 e**, 1.72 mg, 0.0022 mmol; **4**, 1.41 mg, 0.0011 mmol; **6**, 1.55 mg, 0.0022 mmol), phenylacetylene (8.4 μL, 0.074 mmol), diphenylphosphine oxide (15 mg, 0.074 mmol) and 1 mL of toluene. The mixture was stirred at 80 °C, after 120 minutes the solvent was dried under vacuum. ^{1}H NMR of the reaction crude was carried out in $CDCl_3$ to calculate the conversion. The conversion was determined using 1,2-dichloroethane as internal standard.

X-ray crystallography. X-ray data collection of suitable single crystals of compounds **1 a**, **1 e**, **2 a**, **2 b**, **3 a**, **5**, **6** and **7** were done on a SuperNova Single source at offset/far Eos diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2,[36] the structure was solved with the ShelXT[37] structure solution program using Intrinsic Phasing and refined with the ShelXL[38] refinement package using Least Squares minimisation. Details of the structure determination and refinement of compounds are summarized in Table S1 and Table S2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 2026619–2026623 and 2087788–2087790.

Supporting Information

(see footnote on the first page of this article): NMR, MS and IR spectra of compounds, NMR spectra of catalytic experiments and tables with crystallographic data and structure refinement details. Deposition Numbers 2026619 (for **1 e**), 2026620 (for **1 a**), 2026621 (for **2 b**), 2026622 (for **3 a**), 2026623 (for **2 a**), 2087788 (for **5**), 2087789 (for **6**), and 2087790 (for **7**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

This research was supported by Ministerio de Economía y Competitividad (PID2019-111281GB-100) and Gobierno Vasco (IT1880-19). The authors thank SGiker for technical and human support. N. A. is grateful to Diputacion Foral de Gipuzkoa (OF215/2016), and M. A. H. to IKERBASQUE for funding.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Hydrophosphinylation · Organometallic chemistry · Oxidative addition · Rhodium · Secondary phosphine oxides

[1] For recent reviews see: a) P. Sutra, A. Igau, *Coord. Chem. Rev.* **2016**, *308*, 97–116; b) T. Achard, *Chimia* **2016**, *70*, 8–19; c) J. Francos, D. Elorriaga, P. Crochet, V. Cadierno, *Coord. Chem. Rev.* **2019**, *387*, 199–234; d) A. Gallen, A. Riera, X. Verdaguer, A. Grabulosa, *Catal. Sci. Technol.* **2019**, *9*, 5504–5561; e) P. W. N. M. Van Leeuwen, I. Cano, Z. Freixa, *ChemCatChem* **2020**, *12*, 3982–3994.
[2] a) D. M. Roundhill, R. F. Sperline, W. B. Beaulieu, *Coord. Chem. Rev.* **1978**, *26*, 263–279; b) B. Walther, *Coord. Chem. Rev.* **1984**, *60*, 67–105; c) D. Magiera, A. Szmigielska, K. M. Pietrusiewicz, H. Duddeck, *Chirality* **2004**, *16*, 57–64; d) C.-H. Wei, C.-E. Wu, Y.-L. Huang, R. G. Kultyshev, F.-E. Hong, *Chem. Eur. J.* **2007**, *13*, 1583–1593; e) A. Christiansen, L. Chuanzhao, M. Garland, D. Selent, R. Ludwig, A. Spannenberg, W. Baumann, R. Franke, A. Börner, *Eur. J. Org. Chem.* **2010**, 2733–2741; f) T. Achard, L. Giordano, A. Tenaglia, Y. Gimbert, G. Buono, *Organometallics* **2010**, *29*, 3936–3950; g) Y.-C. Chang, W.-C. Chang, C.-Y. Hu, F.-E. Hong, *Organometallics* **2014**, *33*, 3523–3524; h) H. Tavakol, F. Keshavarzipour, *Heteroat. Chem.* **2016**, *27*, 210–220.
[3] G. Manca, M. Caporali, A. Ienco, M. Peruzzini, C. Mealli, *J. Organomet. Chem.* **2014**, *760*, 177–185.
[4] a) X. Jiang, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *J. Org. Chem.* **2004**, *69*, 2327–2331; b) R. González-Fernández, P. Crochet, V. Cadierno, M. I. Menéndez, R. López, *Chem. Eur. J.* **2017**, *23*, 15210–15221.
[5] a) P. A. Donets, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 11772–11775; b) D. Zell, S. Warratz, D. Gelman, S. J. Garden, L. Ackermann, *Chem. Eur. J.* **2016**, *22*, 1248–1252; c) L. V. Graux, M. Giorgi, G. Buono, H. Clavier, *Dalton Trans.* **2016**, *45*, 6491–6502.
[6] a) P. W. N. M. van Leeuwen, C. F. Roobeek, J. H. G. Frijns, G. Orpen, *Organometallics* **1990**, *9*, 1211–1222; b) A. Christiansen, C. Li, M. Garland, D. Selent, R. Ludwig, R. Franke, A. Börner, *Chem. Eur. J.* **2011**, *17*, 2120–2129; c) A. Christiansen, D. Selent, A. Spannenberg, M. Köckerling, H. Reinke, W. Baumann, H. Jiao, R. Franke, A. Börner, *Chem. Eur. J.* **2011**, *17*, 2120–2129; d) P. M. Castro, H. Gulyás, J. Benet-Buchholz, C. Bo, Z. Freixa, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2011**, *1*, 401–407; e) X. Tan, W. Zeng, X. Zhang, L. W. Chung, X. Zhang, *Chem. Commun.* **2018**, *54*, 535—538.
[7] a) E. Rafter, T. Gutmann, F. Löw, G. Buntkowsky, K. Philippot, B. Chaudret, P. W. N. M. van Leeuwen, *Catal. Sci. Technol.* **2013**, *3*, 595–599; b) I. Cano, M. A. Huertos, A. M. Chapman, G. Buntkowsky, T. Gutmann, P. B. Groszewicz, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2015**, *137*, 7718–7727; c) I. Cano, L. M. Martínez-Prieto, B. Chaudret, P. W. N. M. van Leeuwen, *Chem. Eur. J.* **2017**, *23*, 1444–1450.
[8] a) D. S. Glueck, *J. Org. Chem.* **2020**, *85*, 14276–14285; b) K. D. Troev, Reactivity of P–H Group of Phosphorus Based Compounds; Elsevier: Amsterdam, 2017; c) X.-T. Zhu, Q. Zhao, F. Liu, A.-F. Wang, P.-J. Cai, W.-J. Hao, S.-J. Tu, B. Jiang, *Chem. Commun.* **2017**, *53*, 6828–6831; d) V. P. Ananikov, I. P. Beletskaya, *Chem. Asian J.* **2011**, *6*, 1423–1430 and refs. therein; e) J. Green, Fire Retardancy of Polymeric Materials, Marcel Dekker, New York, 2000.
[9] L.-B. Han, N. Choi, M. Tanaka, *Organometallics* **1996**, *15*, 3259–3261.
[10] L.-B. Han, C.-Q. Zhao, M. Tanaka, *J. Org. Chem.* **2001**, *66*, 5929–5932.
[11] a) S. Rooy Van, C. Cao, B. O. Patrick, A. Lam, J. A. Love, *Inorg. Chim. Acta* **2006**, *359*, 2918–2923; b) N. Allefeld, J. Bader, B. Neumann, H. G. Stammler, N. Ignat'ev, B. Hoge, *Inorg. Chem.* **2015**, *54*, 7945–7952.
[12] L.-B. Han, C. Zhang, H. Yazawa, S. Shimada, *J. Am. Chem. Soc.* **2004**, *126*, 5080–5801.
[13] M. Niu, H. Fu, Y. Jiang, Y. Zhao, *Chem. Commun.* **2007**, 272–274.
[14] a) T. Huang, Y. Saga, H. Guo, A. Yoshimura, A. Ogawa, L.-B. Han, *J. Org. Chem.* **2018**, *83*, 8743–8749; b) H. Wang, Y. Li, Z. Tang, S. Wang, H. Zhang, H. Cong, A. Lei, *ACS Catal.* **2018**, *8*, 10599–10605.
[15] C.-Q. Zhao, L.-B. Han, M. Goto, M. Tanaka, *Angew. Chem. Int. Ed.* **2001**, *40*, 1929–1932; *Angew. Chem.* **2001**, *113*, 1983–1986.
[16] A. Gallen, S. Orgué, G. Muller, E. C. Escudero-Adán, A. Riera, X. Verdaguer, A. Grabulosa, *Dalton Trans.* **2018**, *47*, 5366–5379.
[17] A. Christiansen, D. Selent, A. Spannenberg, W. Baumann, R. Franke, A. Börner, *Organometallics* **2010**, *29*, 3139–3145.
[18] X.-B. Wang, M. Goto, L.-B. Han, *Chem. Eur. J.* **2014**, *20*, 3631–3635.
[19] V. Varela-Izquierdo, A. M. Geer, B. de Bruin, J. A. López, M. A. Ciriano, C. Tejel, *Chem. Eur. J.* **2019**, *25*, 15915–15928.
[20] a) C. Martin, S. Mallet-Ladeira, K. Miqueu, G. Bouhadir, D. Bourissou, *Organometallics* **2014**, *33*, 571–577; b) J. Weissmann, L. T. Scharf, V. H. Gessner, *Organometallics* **2016**, *35*, 2507–2515.
[21] R. H. Morris, *Inorg. Chem.* **2018**, *57*, 13809–13821.
[22] a) L. V. Graux, M. Giorgi, G. Buono, H. Clavier, *Organometallics* **2015**, *34*, 1864–1871; b) R. Sylvain, L. Vendier, C. Bijani, A. Santoro, F. Puntoriero, S. Campagna, P. Sutra, A. Igau, *New J. Chem.* **2013**, *37*, 3543–3548; c) M. Zafar, R. Rongala, A. N. Pradhan, K. Pathak, T. Roisnel, J. F. Halet, S. Ghosh, *Dalton Trans.* **2019**, *48*, 7413–7424.
[23] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76; *Angew. Chem.* **2002**, *114*, 50–80.
[24] B. Olgemoller, W. Beck, *Inorg. Chem.* **1983**, *22*, 997–998.
[25] a) M. A. Garralda, R. Hernandez, L. Ibarlucea, E. Pinilla, M. R. Torres, M. Zarandona, *Organometallics* **2007**, *26*, 1031–1038; b) V. San Nacianceno, S. Azpeitia, L. Ibarlucea, C. Mendicute-Fierro, A. Rodriguez-Dieguez, J. M. Seco, E. San Sebastian, M. A. Garralda, *Dalton Trans.* **2015**, *44*, 13141–13155; c) S. Azpeitia, M. Barquin, C. Mendicute-Fierro, M. A. Huertos, A. Rodriguez-Dieguez, J. M. Seco, E. San Sebastian, L. Ibarlucea, M. A. Garralda *Dalton Trans.* **2019**, *46*, 3300–3313.
[26] a) J. A. S. Duncan, T. A. Stephenson, M. D. Walkinshaw, D. Hedden, D. M. Roundhill, *J. Chem. Soc. Dalton Trans.* **1984**, 801–807; b) A. Varshney, G. M. Gray, *J. Organomet. Chem.* **1990**, *391*, 415–429; c) C. G. Arena, F. Nicolo, D. Drommi, G. Bruno, F. Faraone, *J. Chem. Soc. Dalton Trans.* **1996**, 4357–4363.
[27] E. Y. Y. Chan, Q.-F. Zhang, Y.-K. Sau, S. M. F. Lo, H. H. Y. Sung, I. D. Williams, R. K. Haynes, W.-H. Leung, *Inorg. Chem.* **2004**, *43*, 4921–4926.
[28] a) R. P. Sperline, W. B. Beaulieu, D. M. Roundhill, *Inorg. Chem.* **1978**, *7*, 2032–2035; b) K. R. Dixon, A. D. Rattray, *Inorg. Chem.* **1977**, *16*, 209–211; c) D. E. Berry, G. W. Bushnell, K. R. Dixon, *Inorg. Chem.* **1982**, *21*, 957–960.
[29] H. Werner, T. N. Khac, *Angew. Chem. Int. Ed.* **1977**, *16*, 324–325; *Angew. Chem.* **1977**, *89*, 332–333.
[30] a) C. J. Den Reijer, H. Rüegger, P. S. Pregosin, *Organometallics* **1998**, *17*, 5213–5215; b) D. García-Pérez, C. López, R. M. Claramunt, I. Alkorta, J. Elguero, *Molecules* **2017**, *22*, 2003.
[31] M. A. Garralda, *Dalton Trans.* **2009**, 3635–3645.
[32] a) M. Barquín, M. A. Garralda, L. Ibarlucea, C. Mendicute-Fierro, E. Pinilla, V. San Nacianceno, M. R. Torres, *Organometallics* **2011**, *30*, 1577–1587; b) N. Almenara, L. Ibarlucea, C. Mendicute-Fierro, J. M. Seco, A. Rodríguez-Diéguez, M. A. Garralda, M. A. Huertos, *Dalton Trans.* **2016**, *45*, 18502–18509; c) S. Azpeitia, U. Prieto, E. San Sebastian, A. Rodríguez-Diéguez, M. A. Garralda, M. A. Huertos, *Dalton Trans.* **2018**, *47*, 6808–6818; d) S. Azpeitia, C. Mendicute-Fierro, M. A. Huertos, A. Rodríguez-Diéguez, J. M. Seco, A. Mota, M. A. Garralda, *Eur. J. Inorg. Chem.* **2021**, 879–891.
[33] a) S. Azpeitia, B. Fernández, M. A. Garralda, M. A. Huertos, *Eur. J. Inorg. Chem.* **2015**, 5451–5456; b) K. T. K. Chan, L. P. Spencer, J. D. Masuada, J. S. J. McCahill, P. Wei, D. W. Stephan, *Organometallics* **2004**, *23*, 381–390; c) K. Polborn, K. Severin, *Eur. J. Inorg. Chem.* **1998**, 1187–1192.
[34] M. E. Richard, K. P. Reese, J. J. Stone, P. D. Pickett, E. S. Tillman, R. A. Stockland Jr., *J. Organomet. Chem.* **2011**, *696*, 123–129.
[35] a) G. Giordano, R. H. Crabtree, R. M. Heintz, D. Forster, D. E. Morris, Di-μ-Chloro-Bis(η^4-1,5-Cyclooctadiene)-Dirhodium(I), John Wiley & Sons, Inc., 2007, pp. 88–90; b) E. W. Abel M. A. Bennett G. Wilkinson, *J. Chem. Soc. A* **1959**, 3178–3182.
[36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[37] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
[38] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8.

Manuscript received: September 6, 2021
Revised manuscript received: October 7, 2021
Accepted manuscript online: October 8, 2021